



Evaluation of Fenton and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments

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ABSTRACT

Fenton treatment ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and different ozone-based Advanced Oxidation Processes (AOPs) (O_3 , O_3/OH^- and $\text{O}_3/\text{H}_2\text{O}_2$) were evaluated as pre-treatment of a mature landfill leachate, in order to improve the biodegradability of its recalcitrant organic matter for subsequent biological treatment. With a two-fold diluted leachate, at optimised experimental conditions (initial pH 3, H_2O_2 to Fe^{2+} molar ratio of 3, Fe^{2+} dosage of 4 mmol L^{-1} , and reaction time of 40 min) Fenton treatment removed about 46% of chemical oxygen demand (COD) and increased the five-day biochemical oxygen demand (BOD_5) to COD ratio (BOD_5/COD) from 0.01 to 0.15. The highest removal efficiency and biodegradability was achieved by ozone at higher pH values, solely or combined with H_2O_2 . These results confirm the enhanced production of hydroxyl radical under such conditions. After the application for 60 min of ozone at $5.6 \text{ g O}_3 \text{ h}^{-1}$, initial pH 7, and 400 mg L^{-1} of hydrogen peroxide, COD removal efficiency was 72% and BOD_5/COD increased from 0.01 to 0.24. An estimation of the operating costs of the AOPs processes investigated revealed that $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was the most economical system ($8.2 \text{ € m}^{-3} \text{ g}^{-1}$ of COD removed) to treat the landfill leachate. This economic study, however, should be treated with caution since it does not consider the initial investment, prices at plant scale, maintenance and labour costs.

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1. Introduction

The generation of leachate remains an inevitable consequence of the practice of waste disposal in sanitary landfills (Wang et al., 2010). Leachate from mature landfills is typically characterised by high ammonium (NH_4^+) content, low biodegradability (low BOD_5/COD ratio) and high fraction of refractory and large organic molecules such as humic and fulvic acids (de Morais and Zamora, 2005; Deng and Englehardt, 2006). In many cases, after treatment by a series of oxidation processes, mature landfill leachate still presents high concentrations of recalcitrant and nitrogenous compounds. Biological processes are not effective for this type of leachate.

In the last two decades, AOPs have been considered an attractive means to eliminate colour, reduce the organic load and improve the biodegradability of recalcitrant contaminants of mature leachates (Deng and Englehardt, 2006; Kochany and Lipczynska-Kochany, 2009; Renou et al., 2008). These processes involve the production

of free radical species, mainly the hydroxyl radical ($\cdot\text{OH}$). The hydroxyl radical is produced from single oxidants such as ozone (O_3), or from a combination of strong oxidants such as O_3 and hydroxide (OH^-), O_3 and hydrogen peroxide (H_2O_2), or ferrous ions (Fe^{2+}) with H_2O_2 (Renou et al., 2008; Rosenfeldt et al., 2006). The combination of Fe^{2+} and H_2O_2 is called Fenton oxidation.

Fenton oxidation has been extensively studied for the treatment of mature landfill leachates. In this advanced oxidation technology, under optimum pH, ferrous ions react with hydrogen peroxide to generate the hydroxyl radical in a very simple and cost-effective manner (Deng and Englehardt, 2006).

Ozone (not decomposed, $\text{pH} < 6$) is a strong oxidiser having high reactivity and selectivity towards organic pollutants such as aromatic compounds (Lucas et al., 2010; Lin et al., 2009). Furthermore, as the standard oxidation potential of the hydroxyl radical ($E_0 = 2.80 \text{ V}$) is much higher than that of ozone ($E_0 = 2.07 \text{ V}$), the use of ozone at high pH (O_3/OH^-) or in a combination with H_2O_2 ($\text{O}_3/\text{H}_2\text{O}_2$) favours the production of hydroxyl radicals and accelerates the removal of recalcitrant organic matter from complex wastewater matrices (Lucas et al., 2010; Tizaoui et al., 2007). Ozonation under alkaline conditions and the combination of ozone with hydrogen peroxide have proved to be effective advanced oxidation processes for landfill leachate (Haapea et al., 2002; Tizaoui et al., 2007).

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Although AOPs are very effective for the treatment of refractory organic pollutants, if they are applied as the only treatment process, they will be expensive. A promising economical alternative to complete the oxidation of refractory compounds is the use of an advanced oxidation technology as pre-treatment to convert initially biorecalcitrant compounds into more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biomass and water (Lin and Kiang, 2003).

This research was conducted to investigate the efficacy and feasibility of Fenton treatment and different ozone-based advanced oxidation processes (O_3 , O_3/OH^- and O_3/H_2O_2) as pre-treatment steps of a mature landfill leachate, in order to improve its biodegradability for subsequent biological treatment. The effects of initial pH, oxidants concentration and reaction time on the performance of each AOP tested were evaluated in terms of COD, total organic carbon (TOC), BOD_5 , nitrogenous compounds and aromaticity. A rough estimate of the operating costs involved in each type of pre-treatment was also performed to compare their economical feasibility.

2. Materials and methods

2.1. Landfill leachate

Landfill leachate was collected from a municipal landfill in the North of Portugal, in operation since 1998. The current treatment plant in the sanitary landfill comprises stabilisation, anaerobic ponds, an anoxic tank, aerated ponds and a biological decantation unit, together with an oxidation tank and two chemical precipitators. However, even after the post-treatment at the end of the process, the leachate still does not meet the maximum allowable nitrogen and organic matter concentrations for direct discharge, according to DL 236/1998, of August 1 (Portuguese Ministry of Environment, 1998). The characteristics of the undiluted leachate are listed in Table 1.

The low value of the BOD_5/COD ratio (0.01) and the high content of nitrogen-ammonium ($N-NH_4^+$), indicate that this leachate is mature and must be rich in refractory compounds. Another important feature of this leachate is the high nitrogen-nitrate ($N-NO_3^-$) content. An economical approach to treat this leachate can be achieved by combining an advanced oxidation process with the degradation of the refractory compounds into biodegradable organic matter, and using these products as a carbon source for removal of nitrogenous compounds in biological processes.

All experiments were carried out with two-fold diluted leachate due to the high nitrate load of the undiluted leachate, since the Fenton treatment or a different ozone-based advanced oxidation process (O_3 , O_3/OH^- and O_3/H_2O_2) would be applied as pre-treatment step, in order to improve the leachate biodegradability for subsequent biological treatment.

Table 1
Landfill leachate characteristics.

Parameter	Value	Emission limit value (DL 236/1998)
pH	3.5 ± 0.1	6.0–9.0
Conductivity ($mS\ cm^{-1}$)	4.45 ± 0.03	–
COD ($mg\ L^{-1}$)	743 ± 14	150
BOD_5 ($mg\ L^{-1}$)	10 ± 1	40
TOC ($mg\ L^{-1}$)	284 ± 6	–
$N-NO_3^-$ ($mg\ L^{-1}$)	1824 ± 103	11
$N-NO_2^-$ ($mg\ L^{-1}$)	0.010 ± 0.002	–
$N-NH_4^+$ ($mg\ L^{-1}$)	714 ± 23	8
$P-PO_4^{3-}$ ($mg\ L^{-1}$)	0.479 ± 0.054	10 ($mg\ total\ P\ L^{-1}$)
VSS ($mg\ L^{-1}$)	79 ± 3	60 ($mg\ TSS\ L^{-1}$)
UV ₂₅₄	2.614 ± 0.023	–

2.2. Fenton treatment procedure

Fenton oxidation experiments were carried out at room temperature ($22 \pm 1\ ^\circ C$) and atmospheric pressure in magnetically stirred batch reactors with two-fold diluted leachate. The pH of the leachate was adjusted using H_2SO_4 95–97% (w/w). The predetermined Fe^{2+} dosage was achieved by adding the necessary amount of solid $FeSO_4 \cdot 7H_2O$. A calculated volume of 35% (w/w) H_2O_2 solution was added in a single step. After the fixed oxidation time (120 min), sodium hydroxide was added to increase the pH above 7 and mixed for 10 min. Stirring was turned off and the sludge was allowed to settle for one hour. Finally the supernatant was centrifuged for 10 min at 10,000 rpm and the samples were analysed. Experiments were conducted in duplicate and the results were averaged.

2.3. Ozonation procedure

Ozonation experiments were performed in an acrylic column, 69.5 cm high and 8.2 cm internal diameter. Ozone was produced from pure oxygen using an ozone generator (Anseros Peripheral Com-AD-02). The ozone and oxygen mixture was continuously introduced into the column through a ceramic diffuser placed at the bottom and 1 L of two-fold diluted leachate was treated for 60 min. The inlet and outlet concentrations of ozone in the gas phase were measured at $\lambda = 254\ nm$ using an ozone analyser (Anseros Ozomat GM-6000-OEM) throughout the experiments. The gas flow rate was $50\ L\ h^{-1}$ and the input ozone concentration was about $0.112\ g\ O_3\ L^{-1}$. The residual gas was vented through the catalytic ozone destruction unit. Effluent samples were withdrawn regularly and analysed.

Ozonation experiments were carried out at adjusted pH values of 7, 9, and 11. These pH values were achieved using sodium hydroxide (NaOH). Advanced oxidation with hydrogen peroxide and ozone was also studied. In these tests the pH of the leachate was adjusted to 7 (Staehelin and Hoigné, 1982) and, before ozone was supplied, H_2O_2 at concentrations of 100, 200 or $400\ mg\ L^{-1}$ was injected in a single step to the column. The samples collected from these experiments were treated with NaOH to quench the reaction of residual H_2O_2 .

All experiments were carried out at room temperature in duplicate and the results were averaged.

2.4. Analytical methods

The leachate was characterised before and after oxidation experiments. COD, BOD_5 , nitrogen-nitrite ($N-NO_2^-$), and nitrogen-ammonium ($N-NH_4^+$) concentrations were determined according to Standard Methods (APHA et al., 1989). It is important to note that during this work, since acidic and basic pH can affect microbial activity, BOD_5 measurements were done after neutralizing the pH of the sample, as recommended in Standard Methods (APHA et al., 1989).

Nitrate (NO_3^-) concentration was measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, $9\ \mu m$, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H_2SO_4) at $0.7\ mL\ min^{-1}$. Column temperature was set at $60\ ^\circ C$ and nitrate was detected by UV at 210 nm. Ultraviolet absorbance at 254 nm (UV₂₅₄) was obtained with a Jasco V-560 spectrophotometer using a 1 cm quartz cell. TOC analyses were performed using a Dohrmann DC-190 TOC Analyser.

3. Results and discussion

The mature landfill leachate was treated in order to decompose its recalcitrant compounds and increase its biodegradability using

different advanced oxidation systems: Fenton treatment, ozone, ozone at alkaline pH and ozone combined with H_2O_2 . The efficiency of the selected methods depends on many factors including the presence of inorganic and organic substances in the leachate, pH, reaction time and oxidants concentration. Treatability studies were carried out to determine the optimum conditions of each process and its effects on biodegradability. Removal of carbonaceous and nitrogenous compounds, and ultraviolet absorbance at 254 nm was also evaluated. The results obtained are useful to select the best-advanced oxidation process and optimum conditions to be applied to the mature landfill leachate before biological treatment. These data might also lead to a better understanding of the chemical oxidation by Fenton oxidation and ozonation, as well as the role of pH, ferrous ion and hydrogen peroxide concentrations and contact time during degradation of recalcitrant wastewater.

3.1. Fenton treatment

Degradation of pollutants by the Fenton process is most effective in acidic environments due to higher production of hydroxyl free radicals ($\cdot OH$) (de Moraes and Zamora, 2005; Kochany and Lipczynska-Kochany, 2009). Optimal pH values reported for conventional Fenton processes for landfill leachate treatment typically range between 2 and 4.5 (Deng and Englehardt, 2006). This is evidenced in Table 2, which reports the results of the process under different initial pH.

In accordance with literature (Deng, 2007; Lopez et al., 2004), pH 3 resulted in the highest COD and TOC removal efficiencies. At lower pH (<3), the COD removal efficiency decreased, primarily due to the lower reaction rate of $[Fe(H_2O)]^{2+}$ and H_2O_2 (Szpyrkowicz et al., 2001), the increased scavenging of $\cdot OH$ by H^+ (Gallard et al., 1998), and/or the inhibition of the reaction between Fe^{3+} and H_2O_2 due to high concentrations of H^+ (Tang and Huang, 1996). By contrast, COD removal efficiency dropped mainly as the pH exceeded 5, due to the increasing rate of auto decomposition of H_2O_2 , deactivation of iron ions into iron oxyhydroxides, the increased scavenging effect of carbonate and bicarbonate on $\cdot OH$, and/or the decreased oxidation potential of $\cdot OH$.

As can be seen in Table 2, the effect of pH on mineralization (TOC removal) is similar to COD removal efficiency, although slightly lower, under the same operating conditions. This phenomenon was observed throughout the Fenton study and is probably related with the accumulation of carboxylic acids as final products (Cañizares et al., 2009). Therefore, further data related to TOC in Fenton treatment will be not shown.

The absorbance at 254 nm (UV_{254}) could represent the degree of aromaticity and unsaturated compounds present in wastewater (Sevimli, 2005). Thus, a decrease in the UV absorbance might reflect a decrease of recalcitrant compounds and an increase in the BOD_5/COD ratio. From Table 2 it can be observed that UV absorbance removal was also favoured at pH 3. The lower COD removal

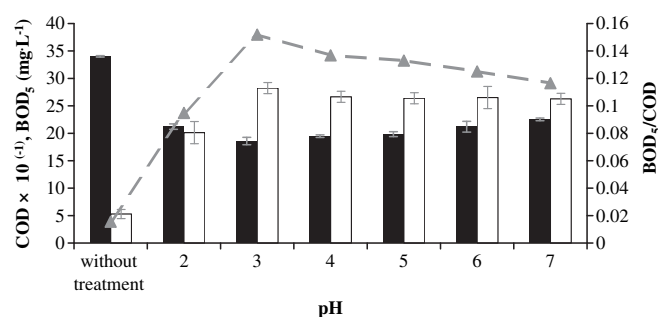


Fig. 1. Effect of initial pH on COD (■), BOD₅ (□) and BOD₅/COD ratio (▲) after 120 min of Fenton treatment at $H_2O_2/Fe^{2+} = 3$, $Fe^{2+} = 4 \text{ mmol L}^{-1}$ and mean initial COD = 340 mg L^{-1} .

compared to UV_{254} removal can be explained by incomplete or partial oxidation of organic materials.

As mentioned before, mature landfill leachate typically presents high concentrations of nitrogenous pollutants, which is undesirable since these compounds are harmful to environment and human health. In our experiments, $N-NO_2^-$, $N-NO_3^-$, and $N-NH_4^+$ concentrations practically did not change after the Fenton process, for the different pH values tested (Table 2). This is in agreement with the results of Wang et al. (2001). Other studies reported that only with high H_2O_2 concentrations in the Fenton process eliminate ammonium and the main by-products are gaseous N_2 and nitrate (Goi and Trapido, 2002). Therefore, further data related to nitrogenous compounds in Fenton treatment will be not shown.

To assess the effect of different pH on leachate biodegradability, BOD₅ measurements were carried out after 120 min of Fenton treatment. The results of COD, BOD₅ and BOD₅/COD as a function of pH are depicted in Fig. 1. It can be seen that Fenton treatment led to an increase in BOD₅ concentrations for all pH values tested. BOD₅ improvement may be attributed to the presence of oxidation by-products with small molecular weights and thus more easily biodegradable, and/or the reduction of the toxicity effect of some organic compounds due to their degradation. BOD₅ increased from 5 to 28 mg L^{-1} at pH 3. The increase in BOD₅ and the decrease in COD led to an increase in the BOD₅/COD ratio. The biodegradability improvement also confirms the occurrence of a partial oxidation process.

Based on the results, further experiments were performed at pH 3.

In Fenton treatment neither H_2O_2 nor Fe^{2+} must be overdosed, to ensure that the maximum amount of $\cdot OH$ radicals is available for the oxidation of organic compounds (Tang and Huang, 1996). Thus, the H_2O_2 to Fe^{2+} molar ratio (H_2O_2/Fe^{2+}) is an important operational parameter to control. The effect of H_2O_2/Fe^{2+} on COD and UV_{254} removal efficiencies was examined under Fe^{2+} concentrations of 1, 2, and 4 mmol L^{-1} . The results are shown in Table 3.

For the three concentrations of ferrous iron tested, the maximum oxidation efficiency occurred at $H_2O_2/Fe^{2+} = 3$. Further increase in this ratio did not show significant removal improvement. This result might be attributed to the scavenging effect of peroxide on the hydroxyl radicals, which presumably became stronger as the ratio H_2O_2/Fe^{2+} increased. Another explanation can be the formation of hydroperoxyl radicals ($HO_2\cdot$), which are less reactive in attacking the recalcitrant compounds in the liquid phase (Kurniawan and Lo, 2009). At a ratio $H_2O_2/Fe^{2+} < 3$, oxidation efficiency decreased, probably because there was not enough hydrogen peroxide to form the hydroxyl radicals. There are a lot of compounds in the leachate that scavenge these radicals, not allowing a significant oxidation to proceed.

Deng (2007) also found an optimal H_2O_2/Fe^{2+} molar ratio of 3 in the Fenton treatment of a mature landfill leachate, although as a pre-treatment.

Table 2

Effect of initial pH on COD, TOC and UV_{254} removal efficiencies; $N-NO_2^-$, $N-NO_3^-$ and $N-NH_4^+$ concentrations in Fenton treatment of a mature leachate (conditions: reaction time = 120 min; $H_2O_2/Fe^{2+} = 3$; $Fe^{2+} = 4 \text{ mmol L}^{-1}$; mean initial COD = 340 mg L^{-1}).

Parameter	Initial pH					
	2	3	4	5	6	7
COD removal (%)	38	46	43	42	38	34
TOC removal (%)	35	42	41	39	37	31
UV_{254} removal (%)	55	62	60	58	53	51
$N-NO_2^-$ (mg L^{-1})	0.003	0.004	0.004	0.003	0.005	0.003
$N-NO_3^-$ (mg L^{-1})	1066	1061	1072	1063	1072	1071
$N-NH_4^+$ (mg L^{-1})	372	361	377	374	386	369

Table 3

Effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and Fe^{2+} concentration on COD and UV_{254} removal efficiencies in Fenton treatment of a mature leachate (conditions: initial pH 3; reaction time = 120 min; mean initial COD = 340 mg L^{-1}).

Fe^{2+} (mmol L^{-1})	Parameter	$\text{H}_2\text{O}_2/\text{Fe}^{2+}$					
		1	1.5	2	2.5	3	3.5
1	COD removal (%)	12	14	15	18	25	22
	UV_{254} removal (%)	14	17	21	22	29	25
2	COD removal (%)	26	29	31	32	36	34
	UV_{254} removal (%)	22	29	34	39	44	40
4	COD removal (%)	29	31	35	41	46	44
	UV_{254} removal (%)	35	43	52	56	62	59

An increase in the initial ferrous iron amount added raised the COD and UV_{254} removal efficiencies (Table 3). This indicates that the leachate did not contain sufficient amount of metal ions to keep the process going at a significant rate. The scavenging effect of Fe^{2+} on hydroxyl radicals was not observed.

The effect of Fe^{2+} concentration on leachate biodegradability was also studied under a fixed $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$. Fig. 2 shows that Fenton treatment resulted in an increase in BOD_5 values for all Fe^{2+} concentrations assayed however, the maximum biodegradability increase occurred at $\text{Fe}^{2+} = 4 \text{ mmol L}^{-1}$.

Further tests were carried out, at initial pH 3, $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$ and $\text{Fe}^{2+} = 4 \text{ mmol L}^{-1}$, to find whether reaction times smaller than 120 min, i.e. the time fixed during the whole investigation, would reduce the extent of leachate oxidation. Table 4 shows that organic matter was rapidly degraded by Fenton treatment. Most organic removal occurred in the first 40 min, after which the change of organic compounds became insignificant. Therefore, 40 min of Fenton treatment for this mature landfill leachate would be enough to obtain approximately the same results as obtained in the full 2 h.

Results of BOD_5 and residual COD indicated that BOD_5/COD ratio increased from 0.01 for the two-fold diluted leachate to 0.15 after 40 min of Fenton treatment, and further reaction did not improve the biodegradability (Fig. 3).

The optimum conditions for the Fenton process studied were as follows: initial pH 3, H_2O_2 to Fe^{2+} molar ratio of 3, Fe^{2+} at 4 mmol L^{-1} , and reaction time of 40 min. For a two-fold diluted leachate, under these conditions, COD removal efficiency was 46%, UV_{254} removal was 62% and BOD_5/COD ratio increased from 0.01 to 0.15.

3.2. Ozonation

To demonstrate the effect of pH on ozonation process, landfill leachate was subjected to ozonation at pH 5.5, 7, 9 and 11 for 60 min. Table 5 presents overall COD, TOC and UV_{254} removals, as well as N-NO_2^- , N-NO_3^- and N-NH_4^+ variations at four different pH values.

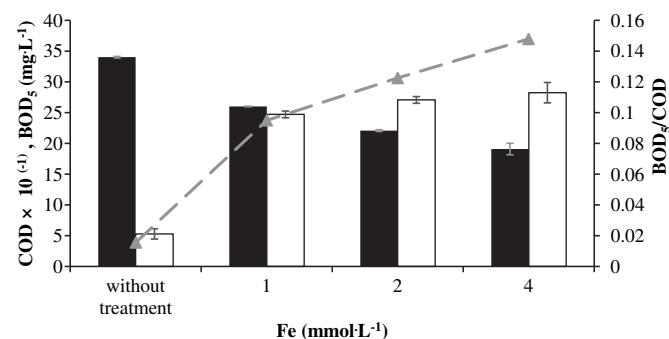


Fig. 2. Effect of Fe^{2+} concentration on COD (■), BOD_5 (□) and BOD_5/COD ratio (▲) after 120 min of Fenton treatment at $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$, initial pH 3 and mean initial COD = 340 mg L^{-1} .

Table 4

Effect of reaction time on COD and UV_{254} removal efficiencies in Fenton treatment of a mature leachate (conditions: initial pH 3; $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$; $\text{Fe}^{2+} = 4 \text{ mmol L}^{-1}$; mean initial COD = 340 mg L^{-1}).

Parameter	Reaction time (min)					
	20	40	60	80	100	120
COD removal (%)	42	46	45	46	46	46
UV_{254} removal (%)	54	61	62	63	63	62

The results of COD, TOC and UV_{254} removal efficiencies indicate that ozonation is more effective at degrading the leachate pollutants under basic pH. It is known that under acidic conditions ozonation allows direct oxidation by molecular ozone, while at high pH values a less selective and faster radical oxidation (mainly hydroxyl radical) becomes dominant as a consequence of OH^- -accelerated O_3 depletion and $\cdot\text{OH}$ radicals production (Langlais et al., 1991). Since the oxidation potential of hydroxyl radicals is much higher than the ozone molecule, indirect oxidation is more powerful than ozone oxidation. Thus, the average efficiency for COD removal increased from 18% at pH 5.5 to 49% at pH 11. Goi et al. (2009) obtained similar results when treating a landfill leachate with COD removal efficiencies of 24, 29 and 41% at initial pH 4.5, 8.1 and 11, respectively, with $2.5 \text{ g O}_3 \text{ h}^{-1}$ and after 240 min of ozonation. TOC removal was lower than COD removal but followed the same tendency. Therefore, further data related to TOC in ozonation will be not shown.

As with Fenton treatment, the lower COD removal compared to UV_{254} removal can be explained by incomplete or partial oxidation of organic materials.

By increasing pH, nitrogen-nitrate concentration increased while nitrogen-ammonium decreased, indicating that ammonium was converted to nitrate. Singer and Zilli (1975) also reported that at higher pH values nitrate formation is enhanced by the direct oxidation of ammonium (in the un-ionized form) by ozone. It would be of interest to determine whether or not N-NH_4^+ should be removed before oxidation once ammonium removal spends ozone. Nitrogen-nitrite concentration moderately increased with the initial pH value and is of no concern.

Fig. 4 depicts the evolution of COD, BOD_5 and BOD_5/COD as a function of pH during ozonation. BOD_5 increased from 5 to approximately 18, 23, 24 and 25 mg L^{-1} at initial pH 5.5, 7, 9 and pH 11, respectively. The biodegradability values obtained at pH 11 are very close to those obtained after 120 min of Fenton treatment at initial pH 3, H_2O_2 to Fe^{2+} molar ratio of 3 and Fe^{2+} at 4 mmol L^{-1} .

The effect of ozone and hydrogen peroxide combination on leachate treatment was explored by adding different amounts of H_2O_2 prior to the start of ozonation, as presented in Table 6. According to Staehelin and Hoigné (1982), the lower limit for the effectiveness of

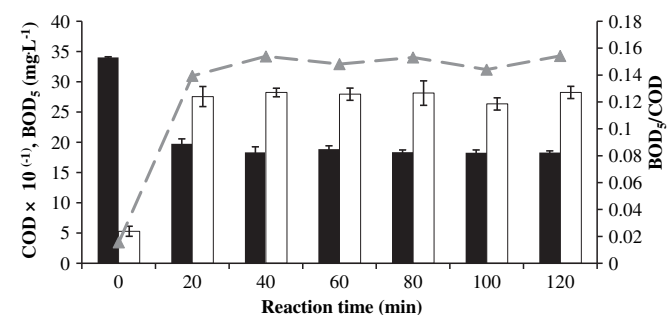


Fig. 3. Effect of reaction time on COD (■), BOD_5 (□) and BOD_5/COD ratio (▲) after Fenton treatment at $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$, initial pH 3, $\text{Fe}^{2+} = 4 \text{ mmol L}^{-1}$ and mean initial COD = 340 mg L^{-1} .

Table 5

Effect of initial pH on COD, TOC and UV₂₅₄ removal efficiencies; N-NO₂⁻, N-NO₃⁻ and N-NH₄⁺ concentrations in ozonation of a mature leachate (conditions: reaction time = 60 min; 5.6 g O₃ h⁻¹; mean initial COD = 340 mg L⁻¹).

Parameter	Initial pH			
	5.5	7	9	11
COD removal (%)	18	27	45	49
TOC removal (%)	12	21	37	41
UV ₂₅₄ removal (%)	42	44	51	57
N-NO ₂ ⁻ (mg L ⁻¹)	0.085	0.111	0.142	0.193
N-NO ₃ ⁻ (mg L ⁻¹)	1109	1135	1150	1174
N-NH ₄ ⁺ (mg L ⁻¹)	335	319	296	269

the H₂O₂/O₃ process is in a pH range of 5–7, therefore the H₂O₂/O₃ process was applied to leachate at pH 7.

The application of H₂O₂/O₃ enhanced the oxidation rate of the landfill leachate compared to ozone alone. These results confirmed that the oxidation of this effluent was mainly due to hydroxyl radicals. COD and aromaticity removals were enhanced from 27% and 44% with ozone only to 72% and 66%, respectively, in the presence of ozone and 400 mg L⁻¹ of hydrogen peroxide, at 5.6 g O₃ h⁻¹ and pH 7.

Some authors (Lin et al., 2009; Tizaoui et al., 2007) report that an increase in hydrogen peroxide concentration will not always improve oxidation. In effect, when the applied hydrogen peroxide dose is above the optimum value, H₂O₂ acts as radical scavenger, suppressing the removal of UV₂₅₄ and COD. In this research, that phenomenon was not observed maybe because the optimum hydrogen peroxide dose was not found. This fact indicates the importance of optimising ozonation for a specific leachate.

Considering nitrogenous pollutants, as is shown in Table 6, nitrogen-nitrate increased and nitrogen-ammonium decreased after 60 min of treatment, confirming that ammonium was oxidised to nitrate. There is not a significant difference between the treatments with O₃ only and with O₃ combined with H₂O₂. Wang et al. (2004) used ozone, and ozone in conjunction with hydrogen peroxide for the treatment of a landfill leachate and found a similar behaviour. Nitrogen-nitrite concentration after ozonation proved to be of no concern.

Results of the effect of O₃ only and H₂O₂/O₃ on biodegradability are presented in Fig. 5. Biodegradability improved in both systems; however, the H₂O₂/O₃ process presented noticeable higher BOD₅/COD values. The higher the H₂O₂ dose, more HO[•] radicals might have been formed and more organic compounds might have been completely oxidised, thus leading to a lower BOD₅ after oxidation with H₂O₂/O₃. The highest BOD₅/COD ratio was attained with the highest H₂O₂ concentration tested (400 mg L⁻¹). Other studies have also reported improvements in BOD₅ and biodegradability after

Table 6

Effect of H₂O₂ concentration on COD and UV₂₅₄ removal efficiencies; N-NO₂⁻, N-NO₃⁻ and N-NH₄⁺ concentrations in ozonation of a mature leachate (conditions: reaction time = 60 min; 5.6 g O₃ h⁻¹; initial pH = 7; mean initial COD = 340 mg L⁻¹).

Parameter	[H ₂ O ₂] = 0 mg L ⁻¹	[H ₂ O ₂] = 100 mg L ⁻¹	[H ₂ O ₂] = 200 mg L ⁻¹	[H ₂ O ₂] = 400 mg L ⁻¹
COD removal (%)	27	41	57	72
UV ₂₅₄ removal (%)	44	48	52	66
N-NO ₂ ⁻ (mg L ⁻¹)	0.111	0.057	0.068	0.071
N-NO ₃ ⁻ (mg L ⁻¹)	1135	1159	1135	1128
N-NH ₄ ⁺ (mg L ⁻¹)	319	291	314	318

leachate treatment of leachate with ozone and hydrogen peroxide (Hagman et al., 2008; Tizaoui et al., 2007).

Table 7 presents of pollutants removal as a function of the ozonation time applied to the landfill leachate.

The results indicate that COD and UV₂₅₄ removal efficiencies increased faster initially, levelling off after 30 min. It can be hypothesised that in the beginning of the reaction, the easily oxidisable substances are removed. As the oxidation continues, the organic compounds that can be easily oxidised became less available and some generated intermediates become increasingly important scavengers of hydroxyl radicals. Further increase in reaction time leads to a slow change in removal rate and a tendency to attain a plateau indicating the presence of recalcitrant compounds. Therefore, it is not always worthwhile to increase the ozone contact time. The continual decrease in absorbance beyond 30 min, when most organic compounds were significantly removed, might be due to continued degradation of intermediates and organic fragments from the organic compounds.

3.3. Comparison of pre-treatments

From the data reported in Sections 3.1 and 3.2, it is possible to assert that both pre-treatments reduced the recalcitrant organic load of the landfill leachate, described in terms of COD, TOC and UV₂₅₄ removal efficiency, and increased the BOD₅/COD ratio. These results indicate that refractory compounds were converted into lower molecular weight substances, which could be easily degraded biologically. Though there was a significant improvement in biodegradability, a BOD₅/COD ratio higher than 0.4, which is the minimum value considered appropriate for the efficient application of a biological treatment (Tchobanoglous and Burton, 1991), was not achieved for all processes tested, emphasising the highly recalcitrant properties of the landfill leachate studied.

The Fenton treatment and ozonation at adjusted pH 9 and pH 11 showed very similar results, excluding the fact that in ozonation

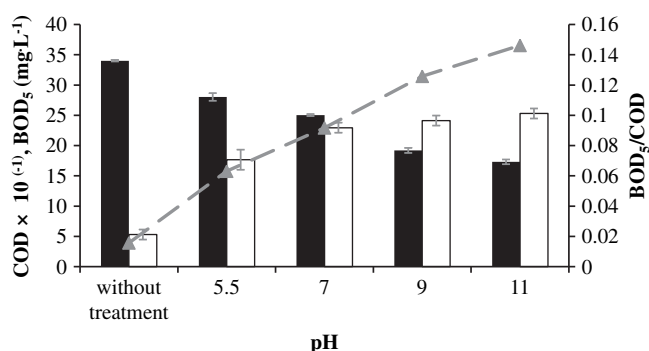


Fig. 4. Effect of initial pH on COD (■), BOD₅ (□) and BOD₅/COD ratio (▲) after 60 min of ozonation at 5.6 g O₃ h⁻¹ and mean initial COD = 340 mg L⁻¹.

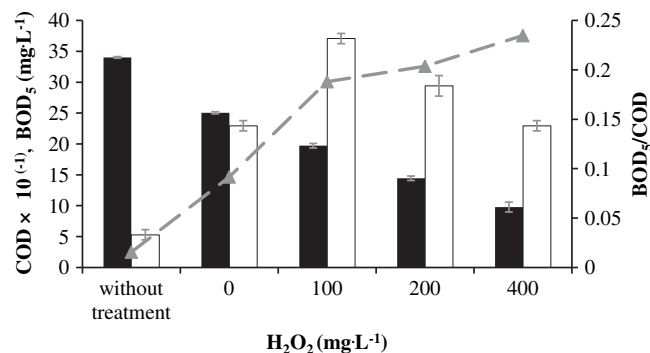


Fig. 5. Effect of H₂O₂ concentration on COD (■), BOD₅ (□) and BOD₅/COD ratio (▲) after 60 min of ozonation at 5.6 g O₃ h⁻¹, initial pH = 7 and mean initial COD = 340 mg L⁻¹.

Table 7

Effect of reaction time on COD and UV₂₅₄ removal efficiencies; N-NO₂⁻, N-NO₃⁻ and N-NH₄⁺ concentrations in ozonation of a mature leachate (conditions: 5.6 g O₃ h⁻¹; initial pH = 7; mean initial COD = 340 mg L⁻¹).

Parameter	Reaction time (min)					
	0	5	15	30	45	60
COD removal (%)	–	15	21	25	27	27
UV ₂₅₄ removal (%)	–	18	23	34	40	44
N-NO ₂ ⁻ (mg L ⁻¹)	0.005	0.067	0.084	0.100	0.108	0.111
N-NO ₃ ⁻ (mg L ⁻¹)	1063	1078	1090	1122	1134	1135
N-NH ₄ ⁺ (mg L ⁻¹)	373	363	351	332	323	319

experiments N-NH₄⁺ was reduced to N-NO₃⁻. The simplicity of operation and design as well as the capital and operating costs of Fenton treatment are very attractive compared with other advanced oxidation processes such as ozonation. However, the process presents some drawbacks such as the requirement of acidification and subsequent neutralisation after oxidation is completed, which increases the salinity of the treated leachate and produces sludge, with the subsequent requirement of sludge disposal, all of which may influence operational costs.

The best COD, TOC and UV₂₅₄ removal efficiencies, and higher BOD₅/COD ratios were achieved by the application of ozone combined with hydrogen peroxide, for concentrations of 200 and 400 mg H₂O₂ L⁻¹.

Probably, coupling the Fenton treatment and ozonation with other treatment technologies would ensure a BOD₅/COD ratio higher than 0.4 before the biological treatment, without significantly increasing operation costs. In the treatment of a landfill leachate, [Goi et al. \(2009\)](#) applied the Fenton treatment followed by ozonation, as well as coagulation combined with the Fenton treatment, and obtained high BOD₅/COD values. [Bila et al. \(2005\)](#) and [Wang et al. \(2009\)](#) also applied ozonation and Fenton treatment, respectively, preceded by the coagulation/flocculation of colloids and found significant biodegradability improvements.

3.4. Operating costs

A rough economic analysis of the operating costs associated to each AOP studied, such as costs of reagents, the costs of reagents required to adjust the pH and energy, was performed. It is important to note that this analysis is just an approximate tool to differentiate the trends in the operating costs associated to the use of each oxidation system. A rigorous economic analysis should consider the initial investment, prices at plant scale, maintenance and labour costs, etc.

It was assumed that the cost of a power unit was 0.09 € kWh⁻¹; the cost of reagents was: 0.179 € kg⁻¹ H₂SO₄, 0.35 € kg⁻¹ NaOH, 0.134 € kg⁻¹ FeSO₄·7H₂O, 0.33 € L⁻¹ H₂O₂ (35%) and 0.08 € m⁻³ O₂; and the operating time was 40 and 30 min for Fenton (at optimum determined conditions) and ozone experiments, respectively. The calculated cost figures are summarised in [Table 8](#).

Table 8

Operating costs for the AOPs studied.

AOP	Operating costs (€ m ⁻³ g ⁻¹ of COD removed)
Fe ²⁺ /H ₂ O ₂	8.2
O ₃ /pH = 5.5	101.1
O ₃ /pH = 7	65.5
O ₃ /pH = 9	36.8
O ₃ /pH = 11	36.3
O ₃ /100 mg H ₂ O ₂ L ⁻¹	41.5
O ₃ /200 mg H ₂ O ₂ L ⁻¹	30.5
O ₃ /400 mg H ₂ O ₂ L ⁻¹	25.6

The results show that the Fenton process offers the lowest operating cost for the treatment of the landfill leachate studied. Considering experiments with ozone, the best results were achieved when hydrogen peroxide was added at concentrations of 200 and 400 mg H₂O₂ L⁻¹.

It must be emphasised that ozonation always requires significantly higher initial investment than the Fenton treatment. However, as stated previously, Fenton oxidation generates sludge, which can be easily separated from the leachate but requires thickening and, consequently, additional investment and operating costs.

Since fine-tuning the operating conditions could considerably change the operating costs obtained, and probably the optimum hydrogen peroxide dose to the H₂O₂/O₃ process was not determined, it can be supposed that at the finest concentration of H₂O₂, the O₃/H₂O₂ process would compete satisfactorily (in terms of operation costs) with the Fe²⁺/H₂O₂ system.

4. Conclusions

The results indicate that Fe²⁺/H₂O₂, O₃/OH⁻ and O₃/H₂O₂ processes, comparatively to ozone at natural and neutral pH values (5.5 and 7), resulted in higher COD, TOC and UV₂₅₄ removal efficiencies and improvement of landfill leachate biodegradability. Although these processes produced significant amendment in leachate quality, a BOD₅/COD ratio of 0.4, considered as a minimum to implement an effective biological treatment, was not achieved, which indicates the refractory nature of the landfill leachate. Ozone in combination with hydrogen peroxide 400 mg L⁻¹ was found to be the best oxidation approach tested. COD removal reached 72% and BOD₅/COD ratio increased from 0.01 to 0.24. For comparison purposes only, estimates of operating costs were calculated. It was found that Fe²⁺/H₂O₂ was the most economical system (8.2 € m⁻³ g⁻¹ of COD removed) to treat the used landfill leachate.

Future work should focus on optimising the mature landfill leachate pre-treatment, including the Fenton treatment and/or ozonation at alkaline pH or combined with hydrogen peroxide, in order to obtain a more biodegradable leachate, which could be followed by biological treatment. Evaluation of costs should also be further investigated prior to practical implementation.

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References

- APHA, AWWA, WPCF, 1989. Standard Methods for the Examination of Water and Wastewater, seventeenth ed. American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollution Control Federation (WPCF), Washington.
- Bila, D.M., Montalvão, A.F., Silva, A.C., Dezotti, M., 2005. Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement. *J. Hazard. Mater.* 117, 235–242.
- Cañizares, P., Paz, R., Sáez, C., Rodrigo, M.A., 2009. Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and Fenton oxidation processes. *J. Environ. Manage* 90, 410–420.
- De Moraes, J.L., Zamora, P.P., 2005. Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. *J. Hazard. Mater.* 123, 181–186.
- Deng, Y., 2007. Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. *J. Hazard. Mater.* 146, 334–340.
- Deng, Y., Englehardt, J.D., 2006. Treatment of landfill leachate by the Fenton process. *Water Res.* 40, 3683–3694.
- Gallard, H., de Laat, J., Legube, B., 1998. Influence du pH sur la vitesse d'oxydation de composés organiques par Fe^{II}/H₂O₂. Mécanismes réactionnels et modélisation. *New J. Chem.* 22, 263–268.

- Goi, A., Trapido, M., 2002. Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study. *Chemosphere* 46, 913–922.
- Goi, A., Veressina, Y., Trapido, M., 2009. Combination of ozonation and the Fenton processes for landfill leachate treatment: evaluation of treatment efficiency. *Ozone Sci. Eng.* 31, 28–36.
- Haapea, P., Korhonen, S., Tuhkanen, T., 2002. Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water. *Ozone Sci. Eng.* 24, 369–378.
- Hagman, M., Heander, E., Jansen, J.L.C., 2008. Advanced oxidation of refractory organics in leachate – potential methods and evaluation of biodegradability of the remaining substrate. *Environ. Technol.* 29, 941–946.
- Kochany, J., Lipczynska-Kochany, E., 2009. Utilization of landfill leachate parameters for pretreatment by Fenton reaction and struvite precipitation – a comparative study. *J. Hazard. Mater.* 166, 248–254.
- Kurniawan, T.A., Lo, W., 2009. Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment. *Water Res.* 43, 4079–4091.
- Langlais, B., Reckhow, D.A., Brink, D.R., 1991. *Ozone in Water Treatment: Application and Engineering*, first ed. Lewis Publishers Inc., Chelsea, MI.
- Lin, A.Y., Lin, C., Chiou, J., Hong, P.A., 2009. O_3 and O_3/H_2O_2 treatment of sulfonamide and macrolide antibiotics in wastewater. *J. Hazard. Mater.* 171, 452–458.
- Lin, S.H., Kiang, C.D., 2003. Combined physical, chemical and biological treatments of wastewater containing organics from a semiconductor plant. *J. Hazard. Mater.* 97, 159–171.
- Lopez, A., Pagano, M., Volpe, A., Di Pinto, A.C., 2004. Fenton's pre-treatment of mature landfill leachate. *Chemosphere* 54, 1005–1010.
- Lucas, M.S., Peres, J.A., Li Puma, G., 2010. Treatment of winery wastewater by ozone-based advanced oxidation processes (O_3 , O_3/UV and $O_3/UV/H_2O_2$) in a pilot-scale bubble column reactor and process economics. *Sep. Purif. Technol.* 72, 235–241.
- Portuguese Ministry of Environment, 1998. Decree-Law no. 236/1998. *Diário da República*. I Série-A 176, 3676–3722.
- Renou, S., Givaudan, J., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: review and opportunity. *J. Hazard. Mater.* 150, 468–493.
- Rosenfeldt, E.J., Linden, K.G., Canonica, S., von Gunten, U., 2006. Comparison of the efficiency of OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2 . *Water Res.* 40, 3695–3704.
- Sevimli, M.F., 2005. Post-treatment of pulp and paper industry wastewater by advanced oxidation processes. *Ozone Sci. Eng.* 27, 37–43.
- Singer, P.C., Zilli, W.B., 1975. Ozonation of ammonia in wastewater. *Water Res.* 9, 127–134.
- Staehelin, J., Hoigné, J., 1982. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.* 16, 676–681.
- Szpyrkowicz, L., Juzzolino, C., Kaul, S.N., 2001. A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. *Water Res.* 35, 2129–2136.
- Tang, W., Huang, C., 1996. 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environ. Technol.* 17, 1371–1378.
- Tchobanoglous, G., Burton, F., 1991. *Wastewater Engineering: Treatment, Disposal and Reuse*, third ed. McGraw-Hill Inc., New York.
- Tizaoui, C., Bouselmi, L., Mansouri, L., Ghrabi, A., 2007. Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems. *J. Hazard. Mater.* 140, 316–324.
- Wang, C., Lee, P., Kumar, M., Huang, Y., Sung, S., Lin, J., 2010. Simultaneous partial nitrification, anaerobic ammonium oxidation and denitrification (SNAD) in a full-scale landfill-leachate treatment plant. *J. Hazard. Mater.* 175, 622–628.
- Wang, F., El-Din, M.G., Smith, D.W., 2004. Oxidation of aged raw landfill leachate with O_3 only and O_3/H_2O_2 : treatment efficiency and molecular size distribution analysis. *Ozone Sci. Eng.* 26, 287–298.
- Wang, P., Lau, I., Fang, H., 2001. Electrochemical oxidation of leachate pretreated in an upflow anaerobic sludge blanket reactor. *Environ. Technol.* 22, 373–381.
- Wang, X., Chen, S., Gu, X., Wang, K., 2009. Pilot study on the advanced treatment of landfill leachate using a combined coagulation, Fenton oxidation and biological aerated filter process. *Waste Manage.* 29, 1354–1358.